

PATENT SPECIFICATION

NO DRAWINGS

1,069,158



1,069

Date of Application and filing Complete Specification: Aug. 17, 1967
No. 33534/64.

Application made in Germany (No. K50619 IXa/57b) on Aug 23, 1967
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Index at acceptance:—G2 H(1J)1, 1JY, 1Y, 3B, 3C7, 3CY, 3Y, 5B, 5D1A, 5D1Y, 5DY, 7Y, 8C, 8G1B, 8GIY, 8G3B, 8G3C, 8G3Y, 8GY, 8Y, 10, 12); C3 1 4C8C, 4C10, 4C16B, 4C16C, 4C17, 4C20D1, 4D3B1, 4D8, 4K9, 4K11 9C8C, 9C10, 9C16B, 9C16C, 9C17, 9C20D1, 9D1A1, 9D1A3, 9D8, 10A, 10C8B, 10C8C, 10C10, 10C16B, 10C16C, 10C17, 10C20D1, 10 10K4, 10K9); G2 M

Int. Cl.:—G 03 g//C 08 g

COMPLETE SPECIFICATION

Developer for Latent Electrostatic Images

We, KALLE AKTIENGESELLSCHAFT, a Body charged with the

ERRATA

SPECIFICATION No. 1,069,158

Page 1, Heading, Date of Application and filing Complete Specification: for "Aug. 17," read "Aug. 17,"

Page 2, line 31, for "produits" read "products"

Page 4, line 3, after "phenyl" insert hyphen

Page 4, line 50, after "a" delete "fine"

THE PATENT OFFICE
10th July 1967

25 ~~remains~~ on the layer as a powder image moreover has a tendency to run during fixing of the image, with the result that the image areas do not have sharp margins.

30 Developers have been proposed which consist of a mixture of organic and inorganic components having approximately the same particle size, but it has not yet been possible to produce a satisfactory resinous toner which acquires a negative charge.

35 Negatively charged organic toners are particularly desirable because organic photoconductive coatings can easily be provided with a positive charge. Latent electrostatic images produced by image-wise exposure of such materials can be satisfactorily developed by a developer containing a negatively

the result of the triboelectric effect and components of the developer having a particle size in the range of 0.2μ — 20μ .

The developer according to the invention is primarily intended for use in developing latent electrostatic images produced image-wise exposure of electrophotographic materials having an organic or inorganic photoconductive coating. It may also be used for developing electrostatic patterns produced by imagewise exposure of a suitable coating provided with a direct-current charge. The basic principles of this method are described in the book "Photoelectrets and the Electrophotographic Process" by V. Fridkin and I. S. Zheludev (1961), Library of Congress Catalog Card Number: 10020, and H. Kallman, B. Rosent

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Int. Cl.:—G 03 g/C 08 g

COMPLETE SPECIFICATION

Developer for Latent Electrostatic Images

We, KALLE AKTIENGESellschaft, a Body Corporate organised according to the Laws of Germany, of 190—196 Rheingaustrasse, Wiesbaden-Biebrich, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

Developers for latent electrostatic images are known which consist of a mixture of particles of an organic material, known as a toner and normally consisting of a synthetic resin, and of larger carrier particles, the particles of the toner and the carrier acquiring opposite charges when they are mixed together. The carrier particles roll off the electrophotographic material during development and are therefore liable to cause damage to the powder image produced by adhesion to the toner which is electrically attracted to the electrophotographic layer. The toner remaining on the layer as a powder image moreover has a tendency to run during fixing of the image, with the result that the image areas do not have sharp margins.

Developers have been proposed which consist of a mixture of organic and inorganic components having approximately the same particle size, but it has not yet been possible to produce a satisfactory resinous toner which acquires a negative charge.

Negatively charged organic toners are particularly desirable because organic photoconductive coatings can easily be provided with a positive charge. Latent electrostatic images produced by image-wise exposure of such materials can be satisfactorily developed by a developer containing a negatively

charged organic toner, the image areas being covered homogeneously by the toner powder. Negatively charged toners are also of commercial importance in connection with the production of enlargements from film negatives. In this case the image areas are not charged, whereas the non-image areas have a negative charge, if, for example, an electrophotographic zinc oxide paper is used. By using a negative toner a reversal to a positive copy is obtained without recourse to a costly intermediate stage.

The invention provides a developer, capable of developing latent electrostatic images, and consisting of a mixture of particles of inorganic material which acquire a positive charge and of particles consisting wholly or partly of a vinylchloride copolymer containing carboxyl groups and which acquire a negative charge, said particles acquiring their respective charges when mixed together as the result of the triboelectric effect and both components of the developer having a particle size in the range of 0.2μ — 20μ .

The developer according to the invention is primarily intended for use in developing latent electrostatic images produced by image-wise exposure of electrophotographic materials having an organic or inorganic photoconductive coating. It may also be used for developing electrostatic patterns produced by imagewise exposure of a suitable coating provided with a direct-current voltage. The basic principles of this method are described in the book "Photoelectrets and the Electrophotographic Process" by V. M. Fridkin and I. S. Zheludev (1961), Library of Congress Catalog Card Number: 61—10020, and H. Kallman, B. Rosenberg:

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"Persistent Internal Polarization" Phys. Rev. 1955, pages 1596—1610.

The following materials may, for example, be used as the inorganic particles which acquire a positive charge:—calcium sulphate, ammonium chloride, sodium chloride, potassium bromide, potassium sulphate, copper sulphate, aluminium-potassium sulphate or sodium sulphate; oxides, for example aluminium oxide, iron oxide, titanium dioxide, zinc oxide or copper oxide; silicates, for example kieselguhr, silica gel, talcum or glass powder; borates, for example sodium metaborate or potassium borate; or carbonates, such as calcium carbonate, magnesium carbonate, potassium carbonate or sodium carbonate. Mixtures of these substances may also be used. The above-mentioned compounds are ground to a fine powder and sieved.

The following substances are suitable for use as the particles which acquire a negative charge:—compounds which are obtained by polymerisation of vinylchloride with vinyl esters of fatty acids, such as acetic acid, propionic acid or butyric acid, and which contain a small proportion of an unsaturated monocarboxylic acid, such as crotonic acid or cinnamic acid or an unsaturated dicarboxylic acid, such as maleic acid, fumaric acid, itaconic acid. Such products are known and commercially available.

The particles of the developer are preferably of size in the range of 1μ — 10μ .

The particles of vinylchloride copolymer containing carboxyl groups may be coloured, e.g. by means of disperse dyes (Colour Index, Vol. 1, pages 1655—1742) such as Celliton dyes, Cibacel dyes and Setacyl dyes, fat dyes, such as Sudan dyes; or dyes of the Naphthol AS series.

Thus 5.0—20.0% by weight of the copolymer of the selected dye may be suspended in water together with the powdered copolymer, and stirred for 2—3 hours at a temperature of 40—70°C. If desired, 2.0—15.0% by weight of an auxiliary agent, for example phenylethylurethane or chlorotoluene, may be added in order to facilitate dyeing and to obtain a deeper colour. Preferably 4.0—6.0% by weight of the auxiliary agent is used. When dyeing is completed the powder is filtered off by suction and washed with water, with or without the addition of natural or synthetic washing agents, and then dried. If desired, the material may thereafter be ground in a ball mill and sieved.

To prepare the developer, one or more of the inorganic positive charging toners, and one or more of the organic resinous negative charging toners are mixed together, preferably in proportions of 1:1 to 20:1 by weight, proportions of 2:1 to 4:1 being preferred.

The developer is applied in known manner to the latent electrostatic image to be de-

veloped and may subsequently be fixed by exposure to solvent vapours or heat. The electrostatic pattern to be developed can be produced in various ways, for example by subjecting a photoconductive layer to a Corona discharge, followed by imagewise exposure to visible, ultra-violet, infra-red or X-rays, by direct electronic formation of an electrostatic pattern on an insulating layer by transfer of such a pattern from another coating or by the method described in the book by Fridkin and Kallmann mentioned above. Furthermore, the developed powder image may be transferred to another material before fixing, in particular by means of a Corona discharge, and may then be fixed on the transfer material.

The developer may also be mixed with iron powder and applied to the image to be developed by using a magnetic rod or a magnetic roller.

If the electrophotographic layer is positively charged, the organic toner will adhere to the unexposed areas of the layer and a positive image of the original will be obtained. Preferably, however, the developer is used for developing a negatively charged layer. In this case, the organic toner adheres to the exposed areas of the layer and a negative image of the original is obtained.

The developer according to the present invention has the advantage that its organic component always retains its negative charge, even if it is used for a prolonged period under conditions of low or high atmospheric humidity. The developer is particularly suitable for the electrophotographic production of enlargements of negative microfilms.

Since the inorganic toner adheres strongly to the borders of the image, and accordingly surrounds the organic toner and prevents it from running, it melts as the result of the heat applied during fixing. Accordingly copies with very sharp edges are obtained, and it is therefore possible to reproduce finer lines or screens than has heretofore been possible.

If the photoconductive coating has been applied to a support which is suitable for litho printing, it is possible to remove the non-image areas of the developed and fixed copy and render them hydrophilic by treatment with an acid or alkaline solution, following which the image areas carrying the hydrophobic toner are inked up with greasy ink. The resulting printing plate is suitable for litho printing.

Considerable advantages are achieved by the use of the above described developer when producing a printing plate. Since the particle size of the two components is approximately the same, and since they generally also have approximately the same specific gravity they are both retained on the image surface. During fixing the inorganic toner

does not melt, but remains on the coating, and when the non-image areas of the coating are removed the inorganic toner is also removed together with the molten organic particles adhering to the coating. Copies with a completely clean background are therefore obtained.

EXAMPLE 1:

5 parts by weight of a black disperse dye Celliton Fast Black BTNU (disperse dye) C.I. Part I, No. 1742, are suspended at 55°C in 1500 parts by weight of water and 5 parts by weight of phenyl-ethyl-urethane are added and the mixture is cooled to 40°C while stirring. 50 parts by weight of a powdery copolymer of 85% by weight of vinylchloride, 14% of vinyl-acetate and 1% of maleic acid are then added in small portions to the cooled suspension, which is then stirred for $\frac{1}{2}$ hour at 40°C and then gradually heated to 65°C over a period of $1\frac{1}{2}$ hours, and finally stirred for another hour at this temperature. After the coloured powder has been filtered by suction it is washed with water and air-dried. The coloured material is then ground in a ball mill and sieved, and particles thereof having a size range of 3 to 5 μ are mixed with kieselguhr particles having a size range of 3 to 5 μ in the proportion 1:4 by weight.

The developer so produced is suitable for the preparation of reversal images. To this end an electrophotographic paper, for example paper coated with zinc oxide, is provided with a negative charge by means of a 6000 volt Corona discharge and then exposed to light under a positive original. The developer is poured over the resulting electrostatic image. The coloured toner powder adheres to the areas affected by light and the resulting visible negative image is fixed by heating. The image has very good contrast and an entirely homogeneous coverage of the image areas.

EXAMPLE 2:

An aluminium plate which has been coated with selenium by vapour-deposition is provided with a positive charge by means of a 6000 volt Corona discharge and exposed to light under a positive original. The resulting electrostatic image is brought into contact with a magnetic rod which has been dipped into a developer mixture of 100 parts by weight of iron powder, 40 parts by weight of aluminium oxide and 10 parts by weight of a copolymer of 85% by weight of vinylchloride, approximately 15% of vinylacetate and less than 1% of a dicarboxylic acid (believed to be maleic acid). This copolymer is sold under the Registered Trade Mark 'Vinnol' E 15/45 M. The developer also contained 0.4 parts by weight of a yellow disperse dye, Setacyl Yellow 4 R.L (Disperse Yellow 34, C.I. Part I, No. 1672) and 0.5

parts by weight of phenyl-ethyl-urethane. The negatively charged yellow toner adheres to the unexposed areas which have a positive charge, so that a positive visible image is obtained. The visible image may be transferred to any desired support, such as paper, aluminium or a plastic material in an electric field and then fixed.

EXAMPLE 3:

100 parts by weight of 'Vinylite' VMCH (Registered Trade Mark), a copolymer of 86% by weight of vinylchloride, 13% of vinylacetate and 1.0% of a compound containing less than 1% of a dicarboxylic acid (believed to be maleic acid), are dissolved at 40°C in 2000 parts by weight of water containing in suspension 12 parts by weight of a black disperse dye Cibacet Diazo Black B (C.I. 11255) and the mixture is stirred for 3 hours at 65°C. A black powder is obtained after drying. This toner is mixed with borax in the proportion of 1:2 by weight. Both constituents have a particle size of approximately 6 μ . The resulting developer is poured over a latent electrostatic image which had been prepared as described in example 1.

The coloured toner adheres to the areas affected by light, and a reversal image of the original is obtained, for example a positive image from a negative original. It is also possible to project an enlargement of a negative microfilm on to the negatively charged electrophotographic paper with the aid of a projector, and to treat the resulting enlarged latent image with the developer just described. A positive enlargement with very good contrast is obtained.

EXAMPLE 4:

30 parts by weight of a copolymer of vinylchloride, vinylacetate and maleic acid (Vilit M) are dissolved at 50°C in a suspension, in 570 parts by weight of water, of 1 part by weight of a black disperse dye Setacyl Black GSP (disperse dye) C.I. Part I, No. 1742, 1 part by weight of a black fat dye, Sudan Black, C.I. 26150, the water containing 4 parts by weight of chlorotoluene. The mixture is stirred for 2 hours at 70°C. The toner obtained upon drying is mixed with an equal weight of purified kieselguhr. The resulting developer is suitable for obtaining direct images on positively charged coatings.

The kieselguhr was purified as follows: 20 parts by weight of a commercially available product are boiled for one hour in 300 parts by weight of 15% hydrochloric acid. After cooling, the kieselguhr is separated by filtration, washed with water and dried. The product is then heated to 600–800°C. Kieselguhr which has been pretreated with trichlorosilane could also be used as an alternative.

An aluminium plate is coated with a mixture of 30 parts by volume (i.e. c.c.) of ethyl-

ene glycol monomethylether and 1 part (i.e. grams) by weight of 2.5-bis-[4'-diethylamino-phenyl(1')] 1.3.4-oxadiazol and 0.8 parts by weight of a copolymer of styrene and maleic acid anhydride having a specific gravity of 1.26—1.28 and a decomposition temperature of 200—240°. After electrostatic charging and image-wise exposure, the resulting latent electrostatic image is developed by means of the developer just described and fixed by subjecting it to trichloroethylene vapour and subsequently heating to 180°C. To convert it into a printing plate, the fixed image is wiped over with a solution containing 10% by weight of monoethanolamine, 5% of sodium metasilicate, 20% of glycerol, 10% of triglycol and 55% of methanol. This removes the coating in the non-image areas together with the kieselguhr deposited thereon. After brief rinsing with water the plate can be inked up with greasy ink and used in an offset machine to produce copies which are free from background.

WHAT WE CLAIM IS:—

- 30 1. A developer, capable of developing latent electrostatic images, and consisting of a mixture of particles of inorganic material which acquire a positive charge and of particles consisting wholly or partly of a vinyl-

chloride copolymer containing carboxyl groups and which acquire a negative charge, said particles acquiring their respective charges when mixed together as the result of the triboelectric effect and both components of the developer having a particle size in the range of 0.2 μ —20 μ .

2. A developer according to claim 1, in which the inorganic particles are of kieselguhr.

3. A developer according to claim 1 or claim 2, in which the particles which acquire a negative charge consists of a copolymer of 85% by weight of vinylchloride, 14% of vinylacetate and 1% of maleic acid.

4. A developer according to any preceding claim, in which the particles have a fine size within the range of 1 μ to 10 μ .

5. A developer according to claim 1, substantially as described herein with reference to any of the foregoing Examples.

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Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to Patents Nos. 975694, 944396, 944395, 944394 and 944393.

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Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

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